

# Morphology of the solid water synthesized through the pathway $D + O_2$ studied by the sensitive TPD technique

M. Accolla,<sup>1,2★†</sup> E. Congiu,<sup>1</sup> G. Manicò,<sup>2★</sup> F. Dulieu,<sup>1</sup> H. Chaabouni,<sup>1</sup> J. L. Lemaire<sup>1</sup> and V. Pirronello<sup>2</sup>

<sup>1</sup>LERMA, UMR8112 du CNRS, de l'Observatoire de Paris et de l'Université de Cergy Pontoise, 5 mail Gay Lussac, F-95000 Cergy Pontoise Cedex, France

<sup>2</sup>Dipartimento di Fisica ed Astronomia, Università degli Studi di Catania, Via Santa Sofia 64, I-95123 Catania, Italy

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## ABSTRACT

We report on an experimental study on the formation of water, through the  $D + O_2$  pathway, on a sample of amorphous solid water, i.e. a realistic analogue of the surface of the interstellar grains of dense clouds. For improving our experimental conditions we use deuterium instead of hydrogen. We obtain, using both Temperature-Programmed Desorption Spectroscopy and Infrared Spectroscopy, that the morphology of the nascent water ice is mostly compact. We compare our results with those obtained previously by Oba et al. and show that the first technique is more effective in probing the morphology of amorphous water ice. We propose that the formation of compact ice is due to the heat of reactions which lead to the formation of water molecules. Water is synthesized, through the  $D + O_2$  pathway, on a film of compact amorphous solid water and on a porous substrate for comparison purposes. We show that in this latter case a gradual compaction of the sample takes place upon formation of new water molecules. We compare this reduction of water ice porosity with that one obtained by Accolla et al., due to recombination of deuterium atoms sent on the surface of an amorphous porous ice sample, and show that the compaction of the sample as a consequence of the water formation appears clearly more efficient.

**Key words:** astrochemistry – methods: laboratory – dust, extinction – ISM: molecules.

## 1 INTRODUCTION

The space between the stars is far from being empty. Ions, atoms and molecules in the gas phase and small solid particles, mixed with the gas, constitute the so-called interstellar medium, or ISM. Approximately, 7 per cent of the mass of our Galaxy, within 15 kpc of the centre, is in the form of interstellar gas, mostly hydrogen and helium (Draine 2011). This gas is not uniformly diffused, instead it aggregates into structures known as interstellar clouds. In diffuse clouds, which are structures with number densities around 100 hydrogen nuclei  $\text{cm}^{-3}$  and temperatures around 50 K, the gas is mainly in atomic form, few molecules are present. In dense interstellar clouds instead, where the number of hydrogen nuclei  $\text{cm}^{-3}$  is higher than  $10^3$ , despite the low number densities and temperatures (10–50 K) a rich chemistry takes place and the dust grains are coated with ‘mantles’ composed of molecular ices, mainly water (Draine 2011). Water has been detected, by infrared (IR) observations, both

in gaseous and solid form (Gibb et al. 2004; Pontoppidan, van Dishoeck & Dartois 2004; Dartois 2005). In gas phase, water may form through the following reaction scheme (Duley & Williams 1984):



which can be summarized as  $H_2 + O + \text{cosmic rays} \rightarrow H_2O$ . As already said, water is the main constituent of the mantles of dust grains in the interstellar dense clouds. Solid water has been detected through the strong broad-band at  $3.07 \mu\text{m}$  due to the O–H stretching mode. Laboratory IR spectra put in evidence that the observed line profile at  $3.07 \mu\text{m}$  is well fitted with that one obtained from an amorphous solid water (ASW) sample instead of a crystalline one (Leger et al. 1979). One could suppose that water builds up the

★ E-mail: mario.accolla@uniparthenope.it (MA); gmanico@dmfci.unict.it (GM)

† Present address: Dipartimento di Scienze Applicate, Università Parthenope di Napoli Centro Direzionale, Isola C4, I-80143 Napoli, Italy.

grain mantle by accretion from the gas phase but this process alone is not able to reproduce the observed abundances (Ceccarelli et al. 2007). So water should form ‘in situ’ by surface reactions in which hydrogen and oxygen are involved, as proposed theoretically several years ago by Tielens & Hagen (1982). They proposed three different routes in which water formation starts up from the hydrogenation, respectively, of O, O<sub>2</sub> or O<sub>3</sub>. The first pathway is the simplest: atomic hydrogen and atomic oxygen react together to form OH, then OH forms water by reacting with H (case a) or with H<sub>2</sub> (case b). Cuppen & Herbst (2007) showed that case (a) is the favourite route in diffuse clouds while case (b) is more efficient in dense clouds, where hydrogen is predominantly in molecular form. The first pathway has been studied experimentally by Dulieu et al. (2010) and by Jing et al. (2011). In both experiments, the authors used D instead of H in order to increase the signal-to-noise ratio. Dulieu et al. (2010) studied water formation through the O + D pathway on a porous water ice substrate at 10 K and obtained a high efficiency for the process (about 50 per cent). Jing et al. (2011) explored instead how water formation occurs on bare surfaces, i.e. in conditions which simulate the transition from diffuse to dense clouds. Hydrogenation of O<sub>2</sub> initiates the second possible route of water formation. The reaction scheme is the following:



and



This route has been experimentally confirmed by Miyachi et al. (2008), at a sample temperature of 10 K and by Ioppolo et al. (2008), in the range of temperatures between 12 and 28 K. Also Oba et al. (2009) examined in situ, using IR spectroscopy, formation of H<sub>2</sub>O through codeposition of O<sub>2</sub> and H and showed that compact amorphous water ice is obtained. The formation route of water starting from O<sub>2</sub> is probably more complex than the one proposed here (Cuppen et al. 2010; Chaabouni et al. 2012; Oba et al. 2012), however, it remains the skeleton of the analysis and it is sufficient for the present discussion. The third possible route takes place from hydrogenation of O<sub>3</sub>, the reaction products are O<sub>2</sub> and OH which enable water formation through the previous routes. Tielens & Hagen (1982) showed that O<sub>3</sub> hydrogenation is the most efficient pathway. Mokrane et al. (2009) obtained no activation barrier if the reaction between O<sub>3</sub> and H takes place on a water layer. Romanzin et al. (2011) also studied the reactions O<sub>3</sub> + H, OH + H and OH + H<sub>2</sub> and their main conclusion was that solid O<sub>3</sub> hydrogenation offers a potential reaction channel for the formation of water in space. In this paper, we study experimentally the formation of water through the O<sub>2</sub> + H pathway and we are interested in the morphology of the nascent water layers. In fact, morphology affects the elementary processes which take place on astrophysical ices, like adsorption, diffusion, chemical reactions and desorption of atoms and molecules (Fillion et al. 2009). For example, Amiaud et al. (2007) showed that, upon formation of molecular hydrogen on the surface of non-porous ASW (np-ASW), H<sub>2</sub> released in the gas phase is vibrationally excited; on the contrary, this behaviour is not observed in the case of p-ASW. Congiu et al. (2009) obtained experimental evidence that interstellar molecular hydrogen is formed and then rapidly de-excited on the surface of porous water ice mantles. Besides they demonstrated that the amount of excited nascent hydro-

gen molecules is significantly reduced no matter the morphology of the water ice substrate at 10 K (both on non-porous and on porous water ice) in a regime of high molecular coverage as is the case of dense molecular clouds. Also Hornekaer et al. (2003) obtained that the fate of the 4.5 eV recombination energy of the reaction H + H → H<sub>2</sub> on ASW is highly dependent on film morphology. Manicò et al. (2001) showed experimentally that hydrogen recombination via surface reactions on icy mantles on grains is able to account for H<sub>2</sub> formation in dense cloud environments. The authors affirm that the astrophysical relevance of their result may be closely connected with the porous structure of an amorphous layer. In fact, according to Mayer & Pletzer (1986), physical adsorption of hydrogen on microporous ASW would have the primary effect of volume filling of the micropores and should lead to an enhanced residence time of H and D atoms in addition to an increased probability of encounter and recombination. Therefore, it is first important to understand (a) what is the role of morphology in the gas–ice interaction and (b) what is the morphology of interstellar ices. This latter point is the subject of this paper. ASW can be produced in high-vacuum conditions by slow vapour condensation on a cold substrate if the temperature is below 130 K (Fillion et al. 2009). According to the particular deposition method used, the ice obtained can be porous or compact. In the case in which water vapour fills the entire vacuum chamber (background deposition) and the deposition is slow the morphology of the ice depends strongly on the substrate temperature. In particular background deposition in the temperature range 110–120 K produces compact ice, while at lower temperatures porous ice is grown (Dohnálek et al. 2003). A p-ASW is characterized by microporous structure where O–H dangling groups are present, and they give rise to two weak features at 3720 and 3696 cm<sup>−1</sup> on the wing of the O–H stretching band at about 3300 cm<sup>−1</sup> (Palumbo 2006). These two dangling –OH features are assigned to vibrations of free –OH groups belonging to two-coordinated water molecules in amorphous ice (one hydrogen bond via O and one via H) and three-coordinated water molecules (two hydrogen bonds via O and one via H), respectively (Buch & Devlin 1991; Rowland, Fisher & Devlin 1991). On the contrary, laboratory experiments emphasize that these features are not observed for a compact ice and disappear when the porous ice is annealed to 120 K. According to our knowledge, to date there has been no detection of dangling bonds in the IR spectra of interstellar ices (Keane et al. 2001). This could be interpreted in two ways: (1) interstellar ices have a compact nature and (2) the features related to OH dangling bonds are too weak to be seen in interstellar spectra. The experiments described and discussed in this paper investigate the morphology of the water synthesized through the pathway D + O<sub>2</sub> and the results are compared with those obtained by Oba et al. (2009). Our experiments are performed on realistic grain surface analogues in dense clouds, namely on a film of compact amorphous solid water (c-ASW), but also on a p-ASW for comparison purposes. Actually, in a dense interstellar environment most of the water molecules should be formed directly above a pre-existing ice layer: typical ice thickness ranges between 40 and 100 molecular layers according to Pontoppidan et al. (2003). We have characterized the morphology of the newly synthesized water layer by studying with a quadrupole mass spectrometer (QMS) the thermal desorption of D<sub>2</sub> molecules deposited and adsorbed on to the sample. We show that this method is particularly sensitive to the morphology of an ASW sample. In addition, our samples have been analysed by IR spectroscopy. Our study demonstrates that mass spectroscopy is a very sensitive tool for studying the morphology of the ice, at least for our thin samples. On the contrary, no definitive conclusions can be drawn on the internal structure of the ice by IR

spectroscopy. Anyway, we can conclude that the solid D<sub>2</sub>O water synthesized on a water icy substrate through the pathway D + O<sub>2</sub> has a compact structure. Therefore, our and other laboratory results (Palumbo 2006; Oba et al. 2009; Palumbo et al. 2010; Accolla et al. 2011) seem to suggest that interstellar ices have a prevalent compact nature.

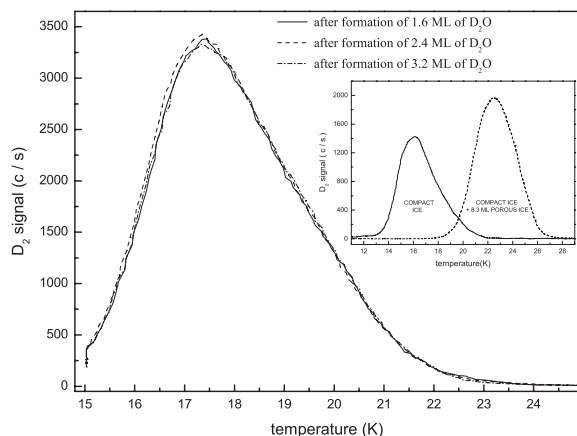
## 2 EXPERIMENTAL METHODS

The experiments were done with the ‘FORMOLISM’ apparatus (i.e. FORMation of MOlecules in the ISM), see Lemaire et al. (2010) and Congiu et al. (2012) for an exhaustive description of the set-up. Essentially, the apparatus permits us to study the chemistry which takes place on surfaces of astrophysical interest in conditions of low pressure and low temperatures and low surface coverage regimes. These conditions are obtained in an ultrahigh vacuum chamber, mainly evacuated by a turbo molecular pump. Typical residual pressure inside the chamber is of the order of 10<sup>-10</sup> mbar and never rise above 2 × 10<sup>-10</sup> mbar during experiments. Inside the main chamber a sample holder is located, consisting of a high conductivity copper circular cylinder and connected to a two stage cryocooler that operates on the principle of the Gifford-McMahon refrigerator cycle. Because of the natural thermal losses the lowest temperature which is possible to reach on the sample is about 8 K. Through an electric resistance it is possible to heat the sample holder. The thermometers and the electric resistance are connected to a controller, Lakeshore 340, that allows us to read the different temperatures and to regulate the sample temperature just by tuning the power of the heating resistance. The chamber also houses a leak valve equipped with a microchannel doser. Once the leak valve is open, a gas – for example water vapour – can diffuse into the chamber via a microcapillary array. In such a way, it is possible to grow interstellar ice analogues on the previously cooled sample surface. Based on the kind of ice we want to grow, two different experimental methods are used as described below. We used two analysis instruments, a movable QMS and an IR spectrometer. The QMS (a HIDEN model) is mounted in the upper part of the chamber and can be translated vertically and rotated. When located in the upper position the QMS is used to analyse chamber gases while if it is moved in the lower position it can either face one of the beams to characterize them or face the sample surface to monitor the desorption rate. The QMS is able to detect partial pressures as low as 10<sup>-14</sup> mbar. Ice samples are also monitored ‘in situ’ by means of Reflection Absorption InfraRed Spectroscopy (RAIRS) using a Fourier Transform InfraRed spectrometer (FTIR) Bruker Tensor 27, which covers the spectral range between 4000 and 700 cm<sup>-1</sup> (2.5–14 μm) with a spectral resolution of 4 cm<sup>-1</sup>. FORMOLISM uses the same architecture devised by Pirronello et al. (1997), i.e. it is equipped with two triple differentially pumped atomic/molecular beam lines that are connected with the main chamber and aimed at the surface of the sample holder. In this way, it is possible to expose the sample to two different species simultaneously with typical atomic/molecular fluxes of 10<sup>12</sup>–10<sup>13</sup> cm<sup>-2</sup> s<sup>-1</sup>. Molecular gases, like hydrogen and oxygen, can be dissociated by means of a microwave cavity housed in the first stage of each beam line. Typical dissociation rates in our apparatus are 70–90 per cent for D<sub>2</sub> and 60–80 per cent for H<sub>2</sub>. These values are measured by means of the mass spectrometer intercepting the beam, just comparing the molecular signal when the microwave discharge is on and when it is off. Our experiments were performed on a substrate of c-ASW ice. The substrate was grown through the microchannel array doser, keeping the copper surface at 120 K. The water vapour was obtained from

deionized water previously purified by several freeze-pump-thaw cycles carried out under vacuum. The c-ASW film was cooled down at 15 K; then O<sub>2</sub> and D (we used deuterium instead of hydrogen to increase the signal-to-noise ratio) were deposited with the following experimental procedure: (1) a very thin film of solid O<sub>2</sub> (~0.2 ML) is deposited on the top of the substrate of c-ASW ice at 15 K; (2) the sample is exposed to 6 min of D atoms (~1.8 ML) and then the temperature of the sample is increased up to 30 K (in this way, we were able to completely remove both the molecular deuterium which form when two atoms of D meet together and undissociated D<sub>2</sub> molecules coming directly from the beam); (3) the sample is cooled again to 15 K and the porosity of the irradiated sample is checked. In practice, the ice is exposed to 30 s of D<sub>2</sub> flux (~0.15 ML of D<sub>2</sub>) and then heated to 30 K using a linear temperature increase (10 K min<sup>-1</sup>) and monitoring in the meanwhile the desorption rate of D<sub>2</sub> (Accolla et al. 2011). The three steps described are iterated many times; we have evaluated that at the end of each iteration we grew on the sample 0.8 ML of D<sub>2</sub>O ice. The procedure followed in the experiments on a porous ice substrate is almost the same used for the compact sample, except that in this case a film of porous ice is grown over a thick compact ice layer. The thickness chosen was 5 ML, which is the thinnest that shows 100 per cent of porous ice energy distribution as shown by Fillion et al. (2009). To summarize, 100 ML of c-ASW have been grown on the copper sample holder at 120 K, then the sample holder was cooled down to 10 K and 5 ML of p-ASW were grown on it. On the so obtained sample we iterated the following steps: deposition for 1 min of 0.2 ML of O<sub>2</sub>, exposure to D atoms for 6 min, heating up to 30 K and cooling down to 10 K, exposure to D<sub>2</sub> molecules for 30 s, temperature-programmed desorption (TPD) up to 30 K.

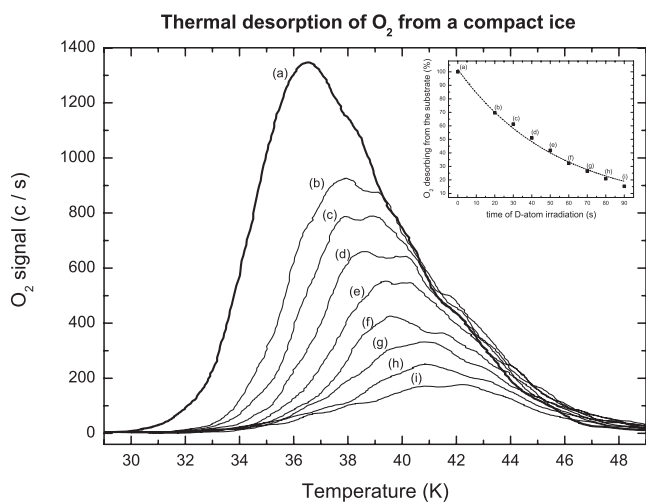
## 3 RESULTS AND DISCUSSION

The iteration of the three steps described in the previous section enable us to study the morphology of the sample as the solid water synthesized is gradually formed on the c-ASW substrate. For several reasons (Amiaud et al. 2006), D<sub>2</sub> seems to be the most appropriate molecule for this kind of experiments: first of all, molecular hydrogen diffuses efficiently within the connected network of pores of ASW even at low temperatures, by contrast with other gases. Moreover, D<sub>2</sub> is weakly bound to the surface and its desorption occurs below 30 K: this temperature limit is not high enough to induce severe transformations of the ice structure, that, on the contrary, occurs using the thermal desorption of other species. Therefore, the thermal desorption of molecular hydrogen or deuterium adsorbed on an amorphous ice is particularly sensitive to the morphology of the sample. This appears clearly in the inset of Fig. 1 that shows two TPD spectra relative to D<sub>2</sub> desorption from a np-ASW (solid line) and from a highly p-ASW (dashed line): no significant desorption from the compact surface is measured above 21 K, whereas desorption from the porous surface persists up to 25 K, because the porous ice is characterized by sites with higher binding energy. Therefore, the higher the porosity is, the higher is the temperature at which the desorption rate has its maximum. TPD experiments using D<sub>2</sub> are very sensitive not only to the morphology, but also to the ice thickness (Hornekaer et al. 2005), although to a lesser extent for very thin films like in our case. Fig. 1 shows the results of our experiments, i.e. the thermal D<sub>2</sub> desorption from the sample after the formation of, respectively, 1.6, 2.4 and 3.2 ML of solid D<sub>2</sub>O water through the pathway D + O<sub>2</sub>. We see that, within the experimental uncertainties, the three TPD profiles can be considered identical, and their position supports the idea that D<sub>2</sub> is desorbing from a compact ice

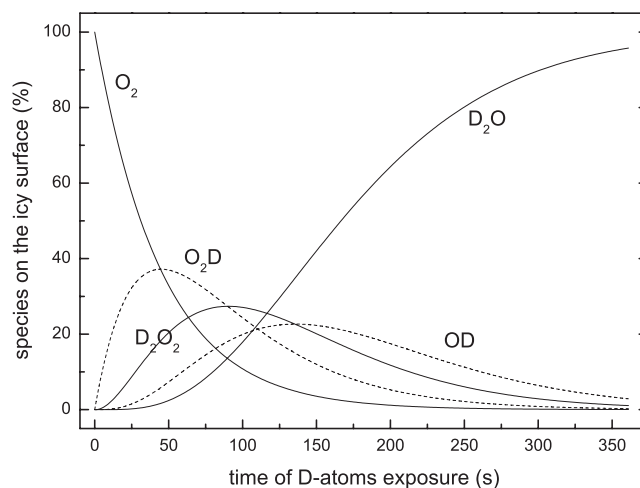


**Figure 1.** TPD spectra of 0.15 ML of  $D_2$  from a compact ice substrate, after formation of  $D_2O$  via  $D + O_2$  pathway. The inset shows the different profiles between  $D_2$  desorption from a compact ice (solid line) and from a porous ice (dashed line): the higher the porosity is, the higher is the desorption temperature.

substrate. In fact, after the synthesis of  $D_2O$  ice, no desorption of  $D_2$  occurs above 22 K, thereby giving the ‘signature’ of  $D_2$  desorption from a compact surface. Therefore, we can certainly declare that the hydrogenation of solid  $O_2$  produces water ice with a compact structure. In our experiments we pay attention that two conditions are satisfied: (1) to maintain a low coverage regime, to assure that  $O_2$  molecules on the solid are isolated and (2) all of the  $O_2$  adsorbed on the surface is converted to water (in order to exclude the presence of intermediate species, as for example  $D_2O_2$ , which might change the properties of  $D_2$  adsorption–desorption processes). For this reason, we have studied how the adsorbed  $O_2$  population decreases as a function of D-atoms exposure. Our results are shown in Fig. 2: the obtained  $O_2$  TPD spectra are a clear evidence that a film of 0.2 ML of solid  $O_2$  is gradually destroyed when irradiated with different doses of D atoms. This set of experiments shows that the  $O_2 + D$  reaction is barrierless, and that the D+D reaction is negligible as long as a measurable fraction (0.05 ML) of  $O_2$  is present on the surface. We also developed a kinetic model in order

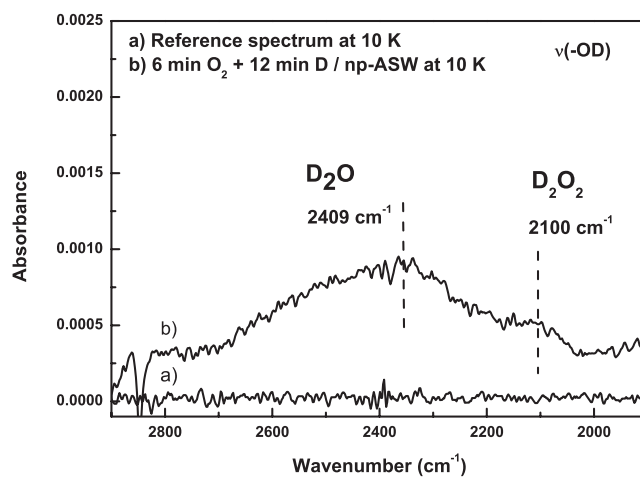


**Figure 2.** Thermal desorption of  $O_2$  from a compact ice.  $O_2$  is gradually destroyed as D-atoms exposure increases. A film of 0.2 ML of solid  $O_2$  is irradiated with (a) 0, (b) 20, (c) 30, (d) 40, (e) 50, (f) 60, (g) 70, (h) 80 and (i) 90 s of D atoms.



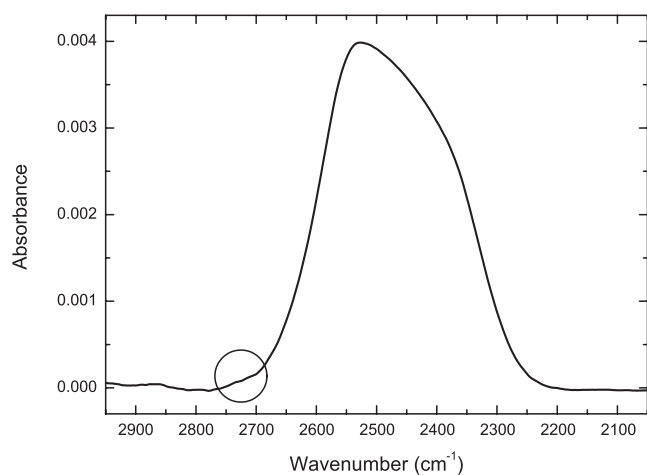
**Figure 3.** Evolution of the species on the surface during the D-atoms exposure of 0.2 ML of solid  $O_2$  as obtained by our kinetic model. The model assumes equivalent probability of formation and no desorption during the D-atoms exposure.

to estimate the evolution of the species on the icy surface during the D-atoms exposure (Fig. 3). We assume as a first approximation that the same probability holds for reactions (6), (7), (8) and (9) (which means no activation barrier and D atoms diffusing quickly) and that no molecule desorbs during the hydrogen exposure, and we find that 360 s of D-atoms exposure on 0.2 ML of solid  $O_2$  are able to form an almost pure substrate of water. The  $O_2$  decrease nicely fits the experimental data of Fig. 2, indicating at least that the first reaction is perfectly reproduced.  $D_2O_2$  and  $D_2O$  ratio obtained at the end of the experiments, indicate that the chemical network is sufficient enough to reproduce qualitatively our results. As already discussed and shown in Fig. 1, our experiments show that the  $O_2 + D$  pathway produces c-ASW on a substrate of compact ice. During the experiments, we also analyse the sample by IR spectroscopy: the acquired IR spectra show the gradual formation of the solid water by the reaction  $D + O_2$ , through the monitoring of the broad O–D stretching band at  $2500\text{ cm}^{-1}$  (Fig. 4). However, these IR spectra are not able to give unequivocal information about the



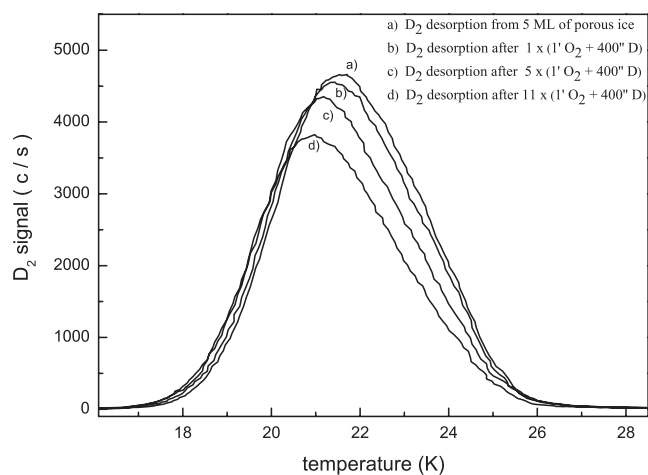
**Figure 4.** IR spectra of  $D_2O$  (0.8–1 ML) formed by  $O_2 + D$  reaction on compact water ice at 10 K. (a) Reference spectrum at 10 K, (b) IR spectrum recorded after the deposition of 6 min  $O_2$  and 12 min D atoms at 10 K on np-ASW  $H_2O$  ice.





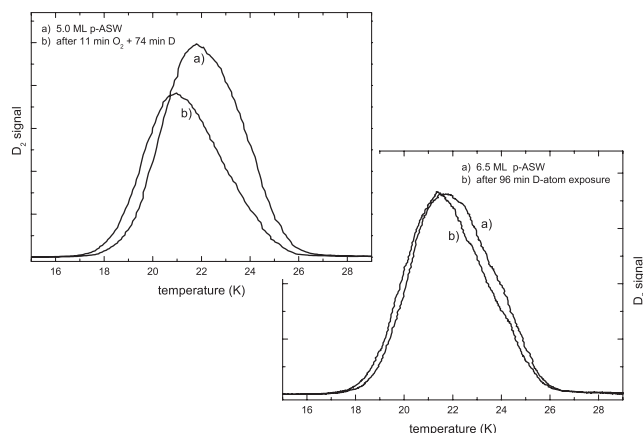
**Figure 5.** IR spectrum of (6 ML) of  $D_2O$  produced by vapour deposition at 10 K on a substrate of compact  $H_2O$  ice and recorded in the 3000–2000  $cm^{-1}$  spectral region corresponding to the  $-OD$  stretching mode of  $D_2O$  molecules. Although the  $D_2O$  ice is a highly porous ice, no features related to dangling bonds (signature of its porosity) appear in the spectrum (circled area).

morphology of the newly formed  $D_2O$  ice because the two bands due to dangling bonds show an intensity below the noise level in the IR signal. Fig. 4 shows the IR spectrum of  $D_2O$  molecules formed by  $O_2 + D$  reaction on compact water ice at 10 K, recorded in the spectral region 2900–1900  $cm^{-1}$  of OD stretching. As shown in the figure, we observe a broad absorption band at 2409  $cm^{-1}$  corresponding to a submonolayer  $D_2O$  water ice and a feature at about 2100  $cm^{-1}$ , which can be attributed to  $D_2O_2$  molecules that are not transformed into  $D_2O$  molecules, but no absorption features between 2734 and 2720  $cm^{-1}$ , belonging to the dangling  $-OD$  of  $D_2O$  molecules, are observed. The IR spectrum shown in Fig. 4 has been obtained using 1 ML of  $O_2$  and 2 ML of D. We can see here again that water formation in our experimental conditions is favoured in contrast to other existing experiments (Ioppolo et al. 2008, 2010; Miyauchi et al. 2008; Oba et al. 2009). To verify the correctness of our observations, we deposited  $\sim 6$  ML of porous  $D_2O$  ice (produced by vapour deposition at 10 K) on a substrate of compact  $H_2O$  ice (Fig. 5). In principle, we should observe two peaks related to dangling bonds in the region between 2734 and 2720  $cm^{-1}$  (the circled area in Fig. 5), but nothing seems to appear in that region. Actually, with the sensitivity of our spectrometer we are not able to distinguish tiny features on the wings of a large and huge band. In a recent paper, Oba et al. (2009) have investigated the formation of both  $H_2O$  and  $H_2O_2$  by codeposition of H atoms and  $O_2$  molecules on a gold plated aluminium substrate. They affirm that the lack of dangling OH bonds in their laboratory spectra after codeposition of  $O_2$  and H indicates the lack of microporous structure in the water ice formed in this way, and therefore its compact nature. Really, as we discussed, the analysis of IR spectra could not be a reliable tool to study the morphology of the ice, at least for thin films. Especially, there is a wide range of intermediate porosities, between the large porosity obtained by depositing films on a 20 K substrate and the compact ice. It leads to different proportion of dangling OH bonds, detectable with IR spectroscopy, even if the relationship between morphology and such a detection is not straightforward. On the contrary, the study of the thermal desorption of  $D_2$  from the ice is able to give very reliable information about the morphology of the sample even for very thin films. Moreover, Oba et al. (2009) suggest that the



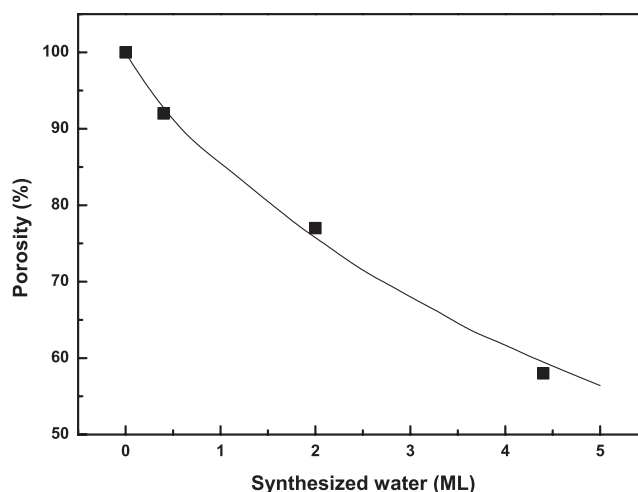
**Figure 6.** TPD spectra of 0.15 ML of  $D_2$  from a porous ice substrate, after formation of water via  $D + O_2$  pathway. The shift towards lower temperatures in the TPD profiles emphasizes the formation of water with a compact structure.

heat of reactions (6), (7) and (8) (respectively, 2.1, 3.7 and 3.9 eV) and that for the H–H recombination (4.5 eV), even if considerably large, do not affect the microscopic structure of amorphous  $H_2O$  ice. This suggestion is considered consistent with the theoretical discussion of Kouchi et al. (1994). By contrast, we have a strong experimental evidence that the energy released upon recombination of hydrogen atoms on the surface of a p-ASW sample leads (as a flux of H atoms landing on the surface is provided) to a gradual compaction of the ice (Accolla et al. 2011); more on this is discussed below. By the way, we observe that in the experiments of Oba et al. (2009) only approximately 2 per cent of H atoms are used for the hydrogenation of  $O_2$  and it is reasonable to assume that  $H_2$  is the most abundant product of the set of reactions involved and therefore it is reasonable to accept that in their experiment there is a possible substantial compaction of the water due to H atom recombination. A similar conclusion cannot be applied in our experiments. As can be seen in Fig. 2, we found that an exposure of 90 s of D atoms is required to destroy 0.2 ML of adsorbed  $O_2$  molecules. By assuming a dissociation efficiency of 55 per cent almost 0.49 ML of D atoms are sent on the surface, then ‘only’ 0.09 ML of D atoms are not used to form water. In this case, the new ice is grown in compact form because of the heating due to the heat of reactions (6), (7), (8) and (9). To confirm that formation of water molecules leads to a change in the morphology of ASW from porous to compact we also investigate the morphology of the water formed through the  $O_2 + D$  pathway on a porous ice sample. We grow at 15 K a porous ice substrate 5 ML thick and we gradually adsorb, as in the previous experiments,  $O_2$  and D on it. In Fig. 6, we show the TPD spectra of  $D_2$  ‘probe’ molecules desorbed from the sample after the formation of 0.4, 2.0 and 4.4 ML of solid water. As it can be seen, a gradual shift towards lower temperatures of the TPD profiles appears as the solid water is progressively formed. We interpret this shift as a demonstration that ice compaction is occurring as Accolla et al. (2011) first showed. Fig. 7 shows the comparison between the two different mechanisms that lead to the gradual compaction of a porous ice sample. Comparing the upper figure (water formation) and the bottom figure (pure D-atoms exposure), we note that the shape of the TPD profiles changes in a different way. In particular, the compaction of the sample as a consequence of the water



**Figure 7.** The two figures show two different mechanisms that lead to the compaction of the sample: the formation of compact ice following D-atoms exposure of solid  $O_2$  upon a porous ice substrate (upper graph) and D-atoms irradiation of a porous ice sample (lower graph).

formation appears clearly more efficient, stressing the likely compact nature of the nascent water. The decrease of the ice porosity can be analysed with the method described in Accolla et al. (2011). In Fig. 6, we can see that the initial porosity of the ice 5 ML thick is reduced about one half after the formation of 4.4 ML of solid water on its surface. In order to explain our experimental results, we propose here a simple model. We suppose that if  $O_2$  and D coming from the beam lead to formation of a water molecule on a porous site, this is transformed into a compact ice site; otherwise if the new molecule is formed on a compact site no change occurs. At the first stages of irradiation, when a higher fraction of the sample still has a porous structure, all the sites are accessible in the matrix of interconnected pores. Because of the gradual compaction of the sample, due to reactions in which  $O_2$  and D are involved, some sites becomes no longer accessible in the structure. We started from a 3D matrix simulating the 5 ML thick p-ASW, each site of the matrix was initially labelled as ‘porous’. To allow the partners of the reactions leading to formation of water to diffuse in the matrix, a random number is extracted and compared with a free parameter representing the percentage of accessible sites. We also take into account the possibility that, because of the energy released by the reactions taking place in our experiment, a volume of the sample, centred on the site where reaction occurs, can become compact, i.e. we consider the number of sites which change to compact ice sites as a second free parameter. The full squares in Fig. 8 represent the decrease of the porosity estimated by calculating the area subtended by each TPD curve for temperatures higher than 23 K. The solid line, instead, shows the decrease of higher binding sites obtained by fitting the experimental data with our model. We find that only the site where the reaction takes place becomes compact if previously porous. Besides we obtain that, when less than 0.5 ML of water molecules are formed, 100 per cent of the sites are accessible to the incoming fluxes, i.e. all sites can be reached by diffusion in the porous structure; on the contrary, when more than 0.5 ML of water molecules are formed, only 63 per cent of the sites should be accessible in order to fit the experimental data. In conclusion, we can say that the porosity of the icy substrate is sharply reduced by the formation of water on its surface. This is like a random growth, possibly with the external sites slightly favoured and with the inner sites which may be less accessible because of the gradual compaction of the porous structure.



**Figure 8.** Decrease of porosity as a function of the solid water synthesized on a porous ice substrate. The full squares show the information about ice porosity extracted by the  $D_2$  TPD profiles in Fig. 6. The solid lines represent the decrease of the ice porosity as estimated by our simple model (see the text for details).

#### 4 CONCLUSIONS

We studied the formation of  $D_2O$  through the pathway  $O_2 + D$  in conditions closely reproducing the surface chemistry occurring on interstellar dust grains in dense regions and showed that the nascent ice has a compact nature instead of porous. Unlike the work of Oba et al. (2009), we used both IR and thermal desorption spectroscopy and, using the technique developed in a previous work (Accolla et al. 2011), we showed that this latter is more efficient in probing the morphology of ASW. Besides we proposed that the formation of compact ice is due to the heat of reactions which lead to the formation of water molecules, i.e. reactions (6), (7), (8) and (9) given above in the text. For comparison purposes, we studied the formation of  $D_2O$  both on c-ASW and p-ASW samples. We showed that in the second case a gradual compaction of the sample takes place upon the formation of new water molecules. We compared this reduction of porosity with those obtained by Accolla et al. (2011), who irradiated a porous amorphous water ice sample with D atoms and observed a gradual compaction upon formation of  $D_2$  molecules, and we showed that the conversion of the sample from porous to compact is much more efficient when new water molecules are formed on it with respect to  $D_2$  formation. This also gives further evidence that the nascent water has a compact structure.

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